polymer reviews

Compatibility and transesterification in binary polymer blends

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Polyester blends have been intensively studied both for industrial application and for academic interest. Properties of these blends are related to their miscibility. It has been found that the miscibility reported for certain blends has been influenced by transesterification. For other polyester pairs miscibility is caused directly and only by interaction of components. The miscibility for a variety of polyester blends, including polyester liquid crystals, is discussed and the relationship between the miscibility and transesterification in the individual blend pairs is detailed in this review.

(Keywords: compatibility; transesterification; binary blends; miscibility; polyesters)

INTRODUCTION

Since the early 1970s, many new pairs of polymers have been found to be miscible. Concomitantly, a large research effort has been launched to try to understand the relationship of polymeric architecture to miscibility. One approach has been the measurement of the Flory–Huggins (χ) parameter by crystallizable blend pairs that have been demonstrated to be miscible. However, the Flory–Huggins χ parameter has been found to be an inadequate representation of the thermodynamics of mixing, because the interaction between components is often found to be composition-dependent[1,2]. The parameter χ is still used, as discussed later, as a first-order description of blend miscibility.

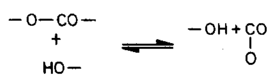
Recently, Coleman *et al.* have proposed a χ_{crit} parameter for prediction of the upper limit for miscibility across the entire composition range[3]. They found that the closer the match of the two non-hydrogen-bonded solubility parameters and the greater the relative strength of the potential intermolecular interactions between the polymer blend components, the greater is the probability of miscibility. This conclusion is axiomatic, and the influence of concentration of any inert diluent is not accounted for[3].

A direct approach is to evaluate the specific interaction between chemical moieties of each chain, as generally required to meet the miscibility requirement of an exothermic heat of mixing. If the enthalpy of mixing is negative, i.e. exothermic, specific interactions between polar groups are expected, and consequently ΔG_{mix} will be negative in spite of the small entropy of mixing[4,5]. The interactions may arise from a variety of mechanisms such as dipole–dipole forces, acid–base attraction[6,7], ion–ion interaction[8] or hydrogen bonding[9]. Barlow and Paul with coworkers have reported a serial study on miscibility of bisphenol A polycarbonate (PC) in polyester blends[10–13]. It is found that, at an optimum density of ester groups in the polyester chain, a maximum interaction between components is achieved, and a miscible blend is formed.

A fascinating feature for blends in the polyester family is the potential for transreaction, also called re-reaction and transesterification. Polyester blends have been studied both for industrial application and for academic interest. Several polyester blends and others with polycarbonate are commercial products: poly(ethylene terephthalate) (PET) with poly(butylene terephthalate) (PBT) is used for moulded automobile parts.

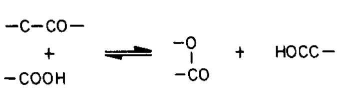
As polyesters readily transesterify, near and above their melting points, interchange reactions commonly occur between constituents[14–25]. This is confirmed from the study of blends of normal (protonated) PET with deuterium-labelled PET by small-angle neutron scattering (SANS). Analysis is based on the difference in coherent scattering length between hydrogen and deuterium chain units. Results show that ester interchange is rapid in the melt and also takes place slowly at 15°C below T_m, resulting initially in the formation of block copolymer consisting of deuterium-labelled and non-labelled segments of PET[24,25].

Kotliar has reviewed interchange reaction involving the condensation polymers, polyesters and polyamides[26]. He discussed the statistics of three different exchange reactions where the chains are terminated by hydroxyl or carboxyl groups. The reactions are intermolecular *alcoholysis*:



$$\begin{matrix}-O-CO- \\ + \\ HO-\end{matrix} \rightleftharpoons -OH + \begin{matrix}CO \\ | \\ O\end{matrix}$$

intermolecular *acidolysis*:



$$\begin{matrix}-C-CO- \\ + \\ -COOH\end{matrix} \rightleftharpoons \begin{matrix}-O \\ | \\ -CO\end{matrix} + HOCC-$$

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and *transesterification*:

$$\begin{matrix} -O-CO- \\ + \\ -CO-O- \end{matrix} \rightleftharpoons \begin{matrix} -O \\ | \\ -CO \end{matrix} + \begin{matrix} CO \\ | \\ O \end{matrix}$$

In the present paper, transesterification is used as a general term to describe all such interchanges including those with polycarbonate.

Transesterification can be readily facilitated, with the following possibilities: it can open a new route to compatibility and preparation of novel copolymers with degrees of randomness and composition; it can lead to a more uniform polymer by minimizing molecular-weight fluctuations in a melt stream during polymerization and processing[27]; and it can provide for chemical healing of polyester laminates[28–30]. In consequence, there is an increasing interest in understanding the interchange reactions that take place between the different functional groups involved in mixtures of polycondensation polymers, viz. polyesters.

As transesterification proceeds, blends convert first to block copolymers and finally to random copolymers. This is irrespective of reaction origin, whether at chain ends or mid-chain. The complex and competitive processes involved, plus the variety of experimental conditions, can result in a range of reaction rates and resultant molecular chain microstructures. The resultant initial block and eventual random copolymers are expected to exhibit enhanced mutual miscibility over the original unreacted components. Moreover, the transreacted chains probably also facilitate and accelerate the compatibilization and reaction of unreacted chains.

Transreaction in polyester blends depends strongly on their initial compatibility and on the blending conditions. This includes temperature, duration of mixing, preparation method, viscosity match and the presence of catalysts[31] and inhibitor[32–35]. Sometimes different conclusions have appeared in the literature concerning blend properties, just because blends were prepared differently. Previously, we have summarized the thermal and mechanical behaviour of binary polyester blends in their crystalline, liquid-crystalline and amorphous phases[36]. In the present review, those binary blends for which transesterification has been demonstrated will be emphasized, in terms of phase behaviour and properties. The amorphous miscibility known for unreacted binary blends is summarized in *Table 1*.

METHODS FOR ANALYSING TRANSESTERIFICATION IN POLYMER BLENDS

On transesterification, the physical properties and the constituents of the system will change due to the production of new components. Several techniques have been used that can detect these changes.

One of the most commonly used techniques is infra-red spectroscopy (i.r.), which originates from molecular vibrations that cause changes in the dipole moment and polarizability of the molecular chains. These spectra are unique to each molecule and therefore reflect the chain structure, especially the concentration of the constituent groups and the intramolecular forces acting among them. In several of the polyester blend studies, new components produced by reaction have been detected by i.r. studies (*Figure 1*)[37–41].

Nuclear magnetic resonance (n.m.r.) is an even more powerful tool for analysis of polymer microstructure and to provide insight about miscibility and the chemical changes within polyester pairs[31,39–45]. The kinetics of transreaction has been studied by this technique[42].

The sensitivity of spectroscopic techniques is insufficient to detect the single bond per chain necessary to start transreaction. Nevertheless, the thermodynamics of interaction between blend components can be sensitively changed from the onset of transesterification. Therefore methods that detect the thermal or thermomechanical behaviour are widely used in such blend studies. Differential scanning calorimetry (d.s.c.), differential thermal

Table 1 Amorphous miscibility evaluation: binary pairs of polyesters and polycarbonate (references are given in square brackets)

Polymer pair	PC	PBT	PET	Kodar	PCL	PETG	Phenoxy	60% PHB–PET	Vectra
PC	–	No [52–60]	No [38, 61–68]	Yes [69, 77, 78, 113]	Yes [51, 71]		No [85b, c]	No [100–103]	
PBT	–	–	Yes [44, 85a]				Yes [77]	Yes & No [75, 91]	
PET	–	–	–				No [78]	No [92–96]	No [107]
PAr	No [75, 77, 80]	Yes [37, 72, 73]	No [74–80]			Yes [77, 83]	No [77a, 84]	Yes & No [123]	
PHMT								No [106]	
PHP	Yes [122]	Yes [122]	No [122]						

The abbreviations are as follows:

Kodar	Cyclohexanedimethanol–tere/isophthalic acid copolyester
PETG	Cyclohexanedimethanol, ethylene glycol, terephthalic acid (1:2:3) copolyester
PHB–PET	*p*-Hydroxybenzoate (PHB) modified PET copolyester
Phenoxy	Poly(hydroxy ether of bisphenol A)
Vectra	Copolyester of hydroxybenzoic acid and hydroxynaphthoic acid
PAr	Copolyester of bisphenol A tere/isophthaloyl (2:1:1)
PHMT	Poly(hexamethylene terephthalate)
PHP	Poly(hydroxy ether of phenolphthalein)

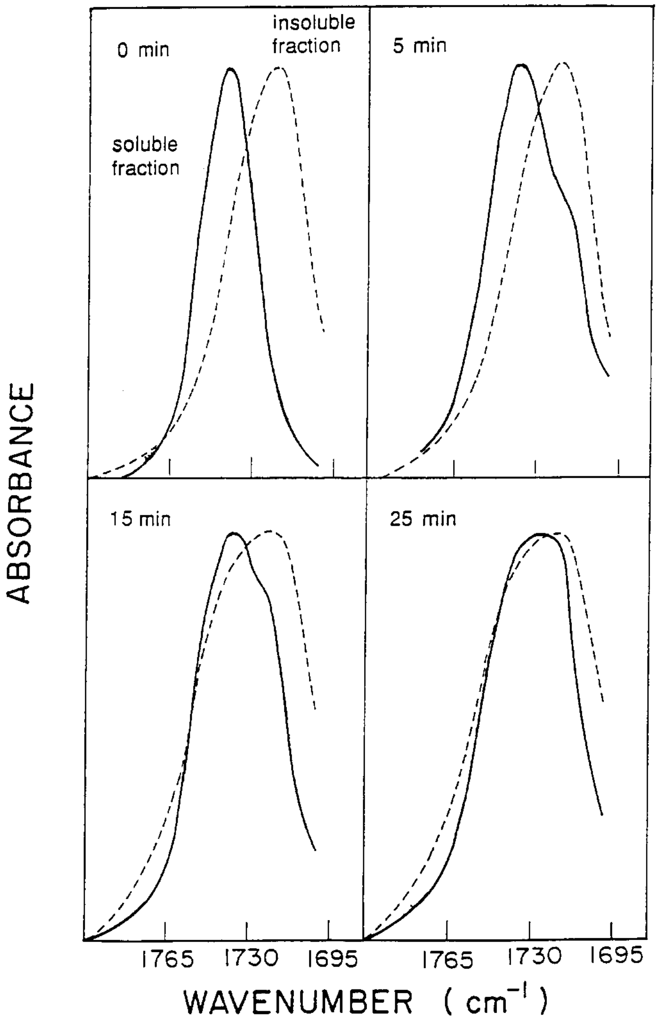


Figure 1 Evaluation of the C=O i.r. stretching bands of PAr/PET samples treated at 297°C after different times: (——) soluble fraction; (----) insoluble fraction[40]

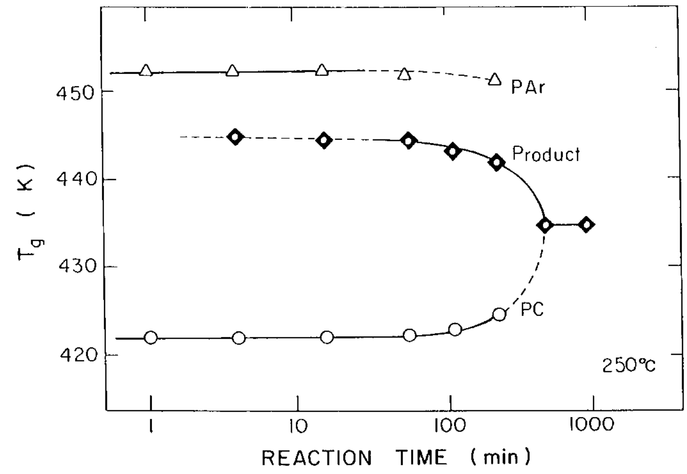


Figure 2 The change of T_g in PAr/PC blends with reaction time[72]

analysis (d.t.a.) and dynamic mechanical analysis (d.m.a.) are used as primary methods for study of the interchange reactions (*Figures 2* and *3*).

The factors determining T_g, the glass transition temperature, are changed on transreaction. A remarkable shift of glass transition is commonly observed for an incompatible pair. A new T_g appears between the two for the original pair.

The T_g can be expressed by the widely used empirical Fox equation[46,47]:

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} \tag{1}$$

where W_i is the weight fraction of component i and T_{gi} is the T_g of component i. More sophisticated equations are available.

The compositional sequence in the polyester chain is changed by reaction. As a result, for crystallizable polymers the melting points (T_m) and fractional crystallinity are depressed. From Flory–Huggins theory, under thermodynamic equilibrium, the melting-point depression can be expressed as follows[48]:

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{RV_2}{\Delta H V_1}\left[\frac{\ln v_2}{x_2} + \left(\frac{1}{x_2} - \frac{1}{x_1}\right)(1 - v_2) + \chi(1 - v_2)^2\right] \tag{2}$$

Here the subscript 1 is identified with the amorphous polymer and 2 with the crystalline polymer; v represents the volume fraction; V is the molar volume of the repeat units; x is essentially the degree of polymerization; T_m is the melting point of the polymer as the excess component, T_m° is the melting point of the perfect polymer crystal; R is the gas constant; ΔH is the heat of fusion per mole of crystalline mers. In polymer blends, both x_1 and x_2 are very large compared to unity. Therefore, equation (2) reduces to[49,50]:

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{RV_2}{\Delta H V_1}\chi(1 - v_2)^2 \tag{3}$$

If $V_1 \approx V_2$, which is often the case, a further simplification is possible:

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{R\chi}{\Delta H}(1 - v_2)^2 \tag{4}$$

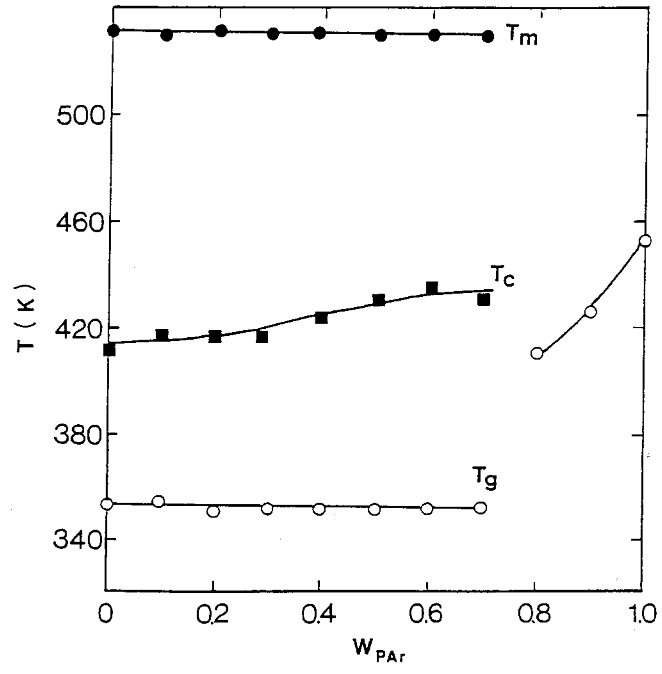


Figure 3 Thermal transitions of PAr/PET blends prepared at 297°C[40]

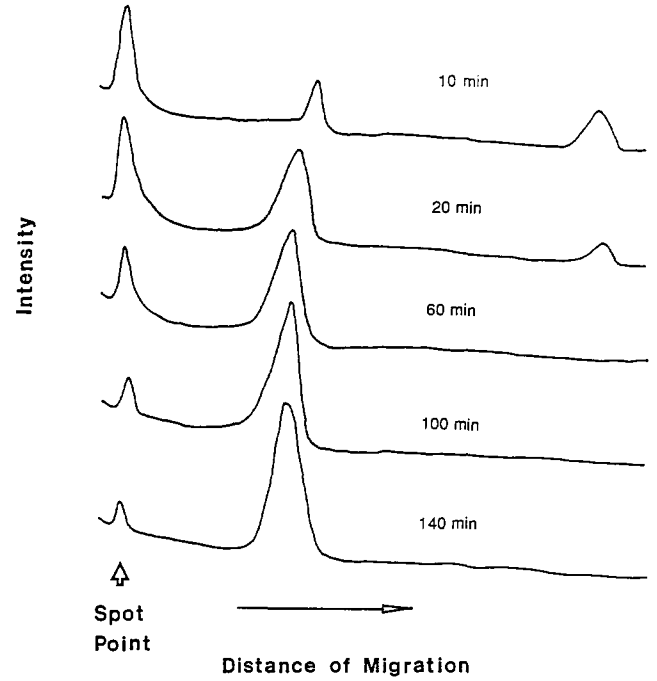


Figure 4 Thin-layer chromatograms of melt-mixed PC/PET (50/50) blends for various times developed with dichloromethane, then followed by a second development with phenol/tetrachloroethane at 270°C[31]

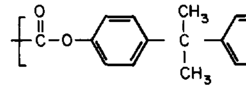
Equations (3) and (4) describe the melting-point depression due to mixing of a crystalline polymer with an amorphous polymer. With this equation, the interaction parameter χ can be obtained. This expression has been applied to transitions in polyesters and to blends where both components may be crystallizable yet still share a miscible amorphous phase[51].

As a consequence of transreaction, the skeletal structure, the molecular weight and the molecular-weight distribution are changed simultaneously. Therefore chromatography can provide an analysis, as by size exclusion. A thin-layer chromatography–infra-red (t.l.c.–i.r.) method has also been used to identify the products of transesterification (*Figure 4*)[31].

BINARY BLEND SYSTEMS

Bisphenol A polycarbonate (PC) binary blends

In this section, the binary blends of various polyesters with bisphenol A polycarbonate (PC), which has the chemical structure as follows, will be discussed. It is normally amorphous with a T_g of about 150°C.



PC

PC/poly(butylene terephthalate) (PBT) blends. The first analysis of PC/PBT blends was made by d.t.a. and d.m.a.[52]. The two components were melt blended in a Brabender Plasticorder for 10 min at 250°C, above the melting point of PBT. Both analyses showed two glass transitions indicative of two amorphous phases. However, these two T_g values in some cases did not correspond to those of the pure components and varied with overall blend composition. The PBT melting point was slightly depressed for blends rich in PC. Moreover, this feature could not be interpreted as a classical depression by a diluent. It was hypothesized that a better explanation was that a reaction had occurred between PC and PBT during the melt processing.

Mercier and coworkers investigated the same blend in the molten state by annealing in an Instron capillary rheometer at a temperature from 224 to 255°C. They observed an exchange reaction that leads to a change from a physical blend to block copolymers and finally to a single-phase random copolymer, as the degree of reaction is increased (*Figure 5*)[39,53–56,58].

It has also been found that the structure of the copolyesters resulting from the exchange reaction is a function of the reaction time, as analysed by i.r. and n.m.r.[43,56,57]. From the mean chain length of the various sequences, as well as the degree of randomness calculated from n.m.r. data, it was concluded that, at short times, the exchange reaction leads initially to the formation of block copolymers. As the reaction proceeds, the sequence distribution in the copolyester becomes statistically random[39].

In order to understand the mechanism of transesterification, a study of a model reaction has been carried out[56]. It was found that bisphenol A terephthalate units and butylene carbonate units were formed in equimolar amounts and the rate constants of the direct (k) and reverse (k') reaction were identical. At equilibrium, a random four-component copolyester was attained. Bernoullian statistics were followed (*Table 2*). From this study, it was concluded that a second-order reversible

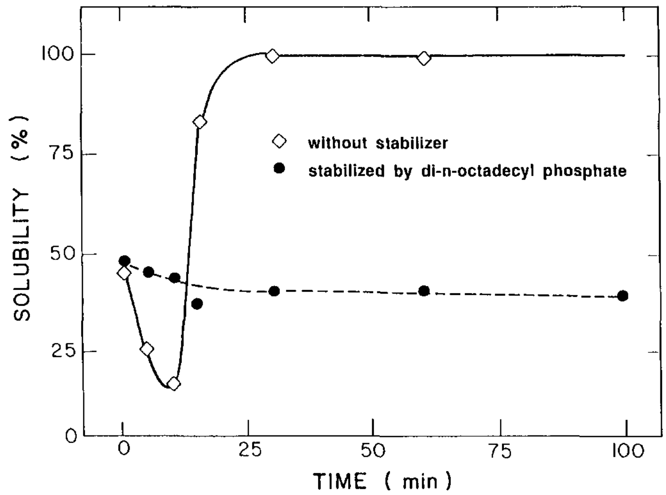


Figure 5 Evolution of the solubility in CH_2Cl_2 of a PC/PBT (50/50) blend as a function of reaction time at 260°C[58]

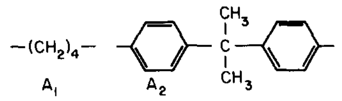
Table 2 Evolution of the average length of butylene (x) and bisphenol A (y) terephthalate sequence in PC/PBT blend (50/50 by weight) as a function of reaction time at 253°C by n.m.r.[39]

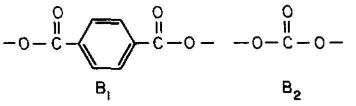
	Reaction time (min)	x	y
Theoretical value for unreacted blend		166	–
Experimental values for copolyester	30	6.46	1.15
	60	3.28	1.42
	100	2.57	
	200		
Theoretical values for statistical copolymer		2.16	1.87

direct ester–ester interchange was the most likely mechanism for the PC–PBT reaction. The overall reaction mechanism can be written as:

$$\underset{\text{PBT}}{-A_1B_1-} + \underset{\text{PC}}{-A_2B_2-} \rightleftharpoons \underset{\text{Copolyester}}{-A_2B_1- + -A_1B_2-}$$

where A_1, A_2, B_1 and B_2 symbolize the following units:





Velden *et al.* used ^{13}C cross-polarization/magic-angle spinning (CP/MAS) n.m.r. and diffuse reflectance Fourier-transform infra-red spectroscopy techniques to confirm transreaction for this blend after heating at 270°C. The amount of transesterification for PC/PBT blends was obtained[43]. This reaction is strongly promoted by temperature. When this blend was prepared in solution, almost complete immiscibility was observed over the entire composition range. But after heating at a temperature higher than the T_m of PBT, copolymer formation was found[59].

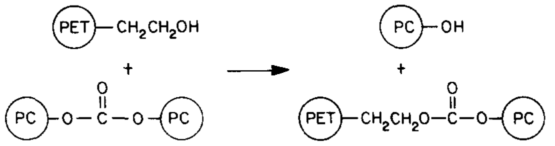
Subsequently, a morphology study of this system has been reported[60]. With increasing amount of PC, the rate of crystallization of PBT was found to be slower and the superstructure of this blend was also changed simultaneously; but the reaction was not mentioned.

PC/poly(ethylene terephthalate) (PET) blends. Conclusions about the behaviour of PC/PET blends are more complex than for PC/PBT. This is because of the range of blends prepared under different conditions reported in individual publications. Complete miscibility for all compositions[61,62] to only partial miscibility[63] for this blend has been reported.

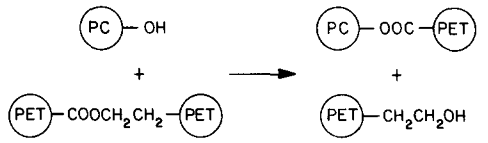
Paul, Barlow and coworkers have stated that, in melt-blended PC and PET, a single T_g was observed for compositions containing more than 60–70 wt% PET, while compositions below this range showed two T_g values. They concluded that PC and PET were completely miscible in the amorphous phase for PET-rich compositions, whereas PC-rich blends separate into two amorphous phases, which apparently contain both components. They suggested that very little if any interchange reactions occur between the ester and carbonate groups during melt mixing[63,64].

Chen and Birley prepared these blends with an extruder at a die temperature of 290°C. The microstructure of PC/PET blends was studied by i.r., d.s.c., d.m.a. and by solution extraction. They found that the blends appeared to contain two amorphous phases over the whole composition range, so that there was no miscibility nor transreaction in their blends[65]. A similar conclusion of immiscibility for this pair was also drawn by Runt and coworkers[66].

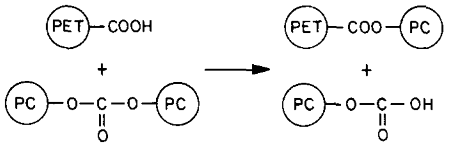
The exchange reaction of PC/PET blends in the molten state (in the range 240–274°C) was carried out by Godard *et al.*[42]. It was found that the transesterification occurred more slowly with PET than PBT, but gives rise also to the four-component copolycondensates in the presence of tetrabutylorthotitanate (TBOT), $Ti(OBu)_4$, as a transesterification catalyst. The reaction was studied by i.r., and by proton and ^{13}C n.m.r. As in their PC/PBT study, an exchange reaction between carbonate and terephthalate groups was found to be the first reaction to take place in PC/PET mixtures. They assumed that the main reaction occurring in molten PC/PET mixtures was also a direct ester–ester interchange, similar to that in the PC/PBT system. This reaction was described by a second-order kinetic model for the molten state. As a consequence of the irreversible decomposition of the ethylene carbonates, the exchange reaction is far from equilibrium[42]. It was also confirmed by selective degradation of PC sequences with piperidine that, when PET and PC were melt mixed at 275°C, they underwent chemical reaction at a low rate when only residue catalyst from PET polymerization was present[67]. The main interchange reactions that may take place between PET and PC according to the three types of reactions proposed by Kotliar[26] are assumed[67] to be *alcoholysis* between hydroxyl end-groups of PET with carbonate groups of PC:



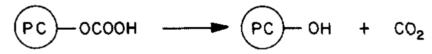
and between phenol end-groups of PC with ester groups of PET:



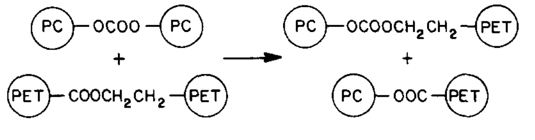
acidolysis between carboxyl end-groups of PET with carbonate groups:



the –OCOOH end-groups formed in this reaction undergoing a degradation according to the following reaction:



plus *transesterification* between ester and carbonate groups:

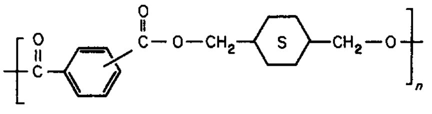


All reactions except the alcoholysis take place during melt mixing of the polyester blends as concluded by the authors[67]. However, there is a major difference between systems. Butylene carbonate formed in molten PC/PBT mixtures seems to disappear at a negligible rate relative to the transesterification rate in the test temperature range ~270°C. On the other hand, ethylene carbonates appearing in PC/PET mixtures are more unstable, and ultimately disappear. So, it was assumed that the decomposition played an important role in transesterification.

More recently, Wang *et al.* have studied the miscibility in PC/PET blends. They found that the system is entirely miscible only after transesterification, as per melt mixing at high temperature, say 300°C, or under longer processing time, as measured by t.l.c.–i.r. and d.s.c. (***Figure 4***). It has been determined that this reaction is activated by the residual catalyst from PET polymerization. Indeed, for a purified PC and PET blend, no exchange reaction could be seen under comparable conditions[31,38]. Conclusions about the role and influence of catalyst on transreaction for this system have been independently reported[42,62]. Similar results were obtained in ref. 68, in which the thermal behaviour by d.s.c. of this blend revealed that the T_g of PET was unaffected by the presence of the PC in the blends and the T_g of PC was overlapped by the cold crystallization, T_c, exotherm of PET.

The divergent conclusions on the miscibility of this system most probably are caused by the residual polymerization catalyst, which can promote reaction. Blending conditions are important. It is therefore not surprising that immiscible blends are obtained on blending after a single extrusion due to insufficient time for reaction[43]. Without reaction, this pair is immiscible.

PC/Kodar blends. This binary system was first reported in 1979[69]. Kodar is a copolymer based on 1,4-cyclohexanedimethanol and a mixture of terephthalic and isophthalic acids:



Kodar

Its T_g by d.t.a. is 86°C. The melting point is in the range of 270–277°C, depending on thermal history of the sample. Quenched samples give values near 277°C, while annealed samples give values near 270°C[69].

By d.t.a. and d.m.a., blends were found to have a single T_g over the entire compositional range. It was thus concluded that Kodar blends with PC form a miscible amorphous phase. The experiment was to follow blend characteristics as a function of mixing time at 280°C. The locations of T_g and T_m were independent of reaction time. The role of ester carbonate interchange reactions was deemed unimportant. The Paul–Barlow group concluded that the observed miscible phase formation was due to physical interactions between the blend components[69].

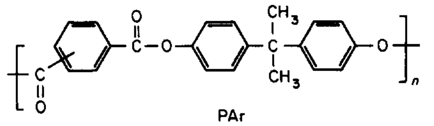
Two years later, an in-depth investigation was carried out by the same group. This indicated that the residual catalyst remaining from the polymerization had a considerable effect on various potential reactions[70]. An added catalyst of 0.2 wt% $Ti(OBu)_4$ was used. Samples were annealed at 177°C for 1 h and then the magnitude of the copolyester melting endotherm was measured. The pure Kodar shows a constant heat of fusion for at least 20 min in the melt state at 277°C, with some evidence of a small decline thereafter. Subsequent time in the melt caused a continued decline in the observed heat of fusion, which is evidence of interchange reactions. After an additional 20 min in the melt, no crystallinity was observed.

As reactions proceed, the blend gradually converts into a copolymer. The speed at which this occurs depends on the amount of titanium catalyst present. A decline in the melting point, an increase of T_g and a change of solubility in chloroform of the blend were observed. To deactivate the titanium catalyst, As_2O_3 or phosphorus stabilizers were used[70]. These compounds were found to be effective for suppressing transreaction and the attendant loss in crystallinity. By both adding and deactivating catalyst, it was confirmed that the miscibility of this blend was aided by transesterification.

PC/poly(ε-caprolactone) (PCL) blends. The miscibility of PC/PCL blends has been investigated by d.s.c.[51,71]. A single T_g has been found across the compositional diagram. The temperature location of this transition was found to be a function only of blend composition, independent of the blending technique. However, no depression was observed in the melting points of either PC or PCL[51,71]. When the 50:50 blend was treated at 250°C for greater than 15 min, a gel was obtained that could only be swollen in CH_2Cl_2, indicating that a crosslinking reaction had taken place. As characterized by *FT*i.r., ^1H and ^{13}C n.m.r., it was found that transesterification did not predominate. Extraction, dissolution, turbidimetric titration and n.m.r. all point to thermo-oxidative branching reactions causing a gel of the two components[51].

Polyacrylate (PAr) binary blends

PAr is a bisphenol A terephthaloyl–isophthaloyl (2:1:1) copolyester. The ratio of phthalic acids can be varied with the general goal of avoiding crystallinity. The structure of PAr is as follows:



PAr

PAr/PBT blends. Blends have been studied before and after transesterification by thermal and dynamic mechanical testing to determine crystallinity and phase behaviour[72]. Blends prepared by solution precipitation showed a single T_g intermediate between that of the individual polymers, increasing with PAr content. This indicates amorphous miscibility of PAr and PBT. A melting-point depression for PBT crystals was not observed. The melting point of PBT is nearly invariant up to high PAr content. The pure PBT crystallizes by separation from the amorphous miscible PAr/PBT phase.

When blends were held at 250°C for 16 h, transesterification occurred, as shown by higher T_g values than for the corresponding physical blends. Also noted was a marked melting-point depression and less PBT crystallinity at higher PAr content. These results are consistent with reaction of the polymer mixture first to block and finally to random copolymers. This is the only system known to us where a different single T_g is obtained on transreaction for an amorphous miscible polymer pair. New n.m.r. and *FT*i.r. data have been provided recently to confirm the transesterification in these blends[37].

Unusual X-ray diffraction results have been obtained on these blends[73]. The X-ray data are shown to be consistent with a nematic order for the PBT in the blends, which is cybotactic nematic structure having both parallel alignment of chains and correlation of the centres of repeat units.

PAr/PET blends. Blends of PAr and PET, before and after transesterification, have been widely studied[74–80]. Physical blends are phase-separated in their amorphous state, involving a pure PET phase and a mixed phase, rich in PAr. The blends were prepared in chloroform followed by drying and compression moulding. Heating at 280°C for over 16 h yields single-phase blends[74,75]. When this system was investigated in detail, it was confirmed that heat treatment (at 280°C) causes transesterification (*Figure 1*). The thermal treatment of blends results in changes with time in T_m, T_g and T_c of PET. The T_m of PET began to decrease after 15 min and eventually disappeared after 60 min. The T_c for PET increased after 10 min and disappeared after long heating. In contrast, the T_g of PET increased after 10 min at 280°C, approaching an equilibrium value after 10 h. From these data, Kimura and Porter suggested that randomization of the copolymers initially formed proceeds after 10 min with completion after 10 h at 280°C[74,75].

A conclusion similar to that of Kimura and Porter was also obtained by Robeson[77,78]. That is, with minimum time and temperature exposure, polyacrylate exhibits phase separation from PET at >30 wt% PET. After a moderate time at 300°C, adequate ester exchange occurs in PAr/PET blends to yield a single amorphous phase. The activation energy of the ester exchange reaction was determined to be 37 kcal mol^{-1}. There are changes in blend solubility and in the *FT*i.r. spectra with reaction time[40,79]. Blends containing more than 30% PET, on conditioning at 297°C, result in progressive ester exchange. Samples with 10% and 20% PET content required less extreme conditioning and exhibited a single T_g and no PET crystallinity (*Figure 3*). The authors attributed this phase behaviour to the spinodal, and a simulated phase diagram was proposed for PET blend[40].

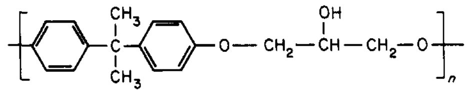
PAr/PC blends. Physical blends of PC/PAr exhibit two amorphous phases: a pure PC phase and a PAr-rich miscible mixed phase. On controlled thermal treatment at 250°C from 1 min to 16 h, reaction progression from block to random copolymer has been traced by d.s.c., ^{13}C n.m.r. and g.p.c.[75,80]. The transreaction between PC and PAr presumably takes place mainly in the mixed phase, producing a new copolymer.

The thermal behaviour of blends showed that, for up to 1 h at 250°C, T_g values of the PC phase and PAr-rich phase remained nearly constant. A new T_g does appear between them at 171°C, attributable to a new copolymer phase. As the transreaction proceeds, the T_g of PAr-rich phase and block copolymer decreases and the T_g of the PC phase increases. At the final step of transreaction (after 4 h), the block copolymers convert to a random copolymer (*Figure 2*).

Completely transreacted blends showed only a single T_g value. It is a few degrees lower than the value calculated by the Fox equation. These new random copolymers are also amorphous, with no tendency to crystallize observable by thermal analysis.

This reaction between PC and PAr, both based on bisphenol A units, has been simulated by studying the reaction between PC and diphenyl terephthalate or isophthalate used as model compounds of a poly(aryl carboxylate). This indicated that transesterification occurs without any catalyst[81].

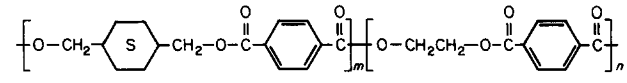
PAr/poly(hydroxy ether of bisphenol A) (phenoxy) blends. The miscibility of PAr/phenoxy blends was investigated under controlled time and temperature conditions[77]. The chemical structure of phenoxy is as follows:



Phenoxy

It was found that its phase behaviour is strongly dependent on temperature. After heating at 270°C, the dynamic mechanical results clearly show phase separation. A sample moulded at 320°C (20 min) yielded a single phase with a modulus plateau above T_g, indicative of crosslinking resulting from transesterification of PAr and phenoxy, as concluded by Robeson[77].

PAr/copolyester of cyclohexanedimethanol, ethylene glycol and terephthalic acid (PETG) blends. The PETG copolyester is a reaction product of terephthalic acid and a mixture of 1,4-cyclohexanedimethanol and ethylene glycol:



PETG

The PAr/PETG blend has been prepared by extrusion and compression moulding at 265–275°C[77]. It was found that single T_g values were observed over the entire composition range, even at minimum time and temperature exposure, in which only minimal ester exchange would be expected. Nonetheless, solution-cast films gave mixed results. In certain cases, the solvent has been found to be critical in regard to phase behaviour of solution-cast films.

It seems that the ester exchange reaction can take place in this system, but miscibility does not depend on this reaction[82]. A contrary result about the transesterification in this blend has been reported, i.e. that the crystalline melting point peak, seen in d.s.c., did not change with blend composition up to 30% by weight PAr, suggesting that the polymer did not appreciably transesterify[83].

Phenoxy binary blends

PET/phenoxy blends. The PET/phenoxy blends appear to be phase-separated when there is no transesterification, as on extrusion just above the PET melting point. The two phases can be resolved. If the same sample is moulded at increasing times at 270°C, changes in the dynamic mechanical results are observed. An initially translucent blend changes to a transparent system upon exposure for 10 min at 270°C. The crystallization rate of PET is increased with phenoxy addition under the conditions of minimum temperature exposure. With longer temperature exposure, the PET crystallization rate is significantly decreased. From T_g studies, a conclusion can be drawn that phenoxy/PET mixtures are phase-separated (perhaps with only limited miscibility). On even mild time–temperature exposure, sufficient transesterification occurs to yield behaviour approaching miscibility[78].

PBT/phenoxy blends. The melt miscibility of PBT/phenoxy blends has been studied[84]. The quenched moulded specimens are transparent. Dynamic mechanical and calorimetric characterization revealed a single and sharp T_g, intermediate between those of the individual constituents. This is evidence of miscibility in the amorphous phase in the non-reacted state. The driving force for the miscibility as given by the authors[84] is the potential specific interactions between the phenoxy hydroxyl (proton donor) and the ester carbonyl of PBT (proton acceptor).

At 250°C for longer time exposure, transesterification in this system leads to the formation of branching and then crosslinking; resulting in a non-fusible product.

PET/PBT blends

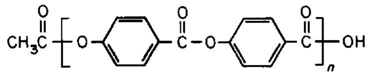
The few papers on PET/PBT blends express contradictory conclusions about transesterification. Stein *et al.* found a single T_g for extruded blends, suggesting that the components are compatible in the amorphous phase[85a]. Studies of the effect of time and temperature on the melt suggested that this reported miscibility was not a consequence of transesterification. The X-ray, d.s.c. and i.r. spectra indicated separate crystals for the two components rather than a co-crystallization[85a].

On the other hand, a direct proof of transesterification between the two polyesters also on blend extrusion was obtained by an n.m.r. study of the difference in chemical shift for the 'quaternary' aromatic carbon[44]. The asymmetrical diester level of the copolyester was estimated from the peak intensities of the copolyester peaks in the ^{13}C n.m.r. spectra. After 6 min, the degree of transesterification reached a maximum of 16% and then the amount decreased with time, owing to the depolymerization of the condensation polymer in the presence of moisture under high temperature and shear conditions as explained by the authors[44].

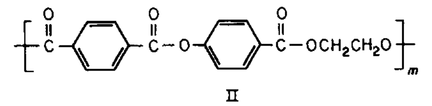
Blends with liquid crystals

Many polymer types that exhibit liquid-crystalline properties have been synthesized and examined in the last decade. Among these, thermotropic liquid-crystalline copolyesters are currently of considerable interest because of their potential applications in, for example, high-strength fibres and films.

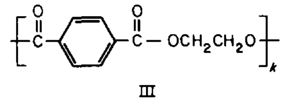
A specific copolyester, a linear PET incorporating a concentration range of the *p*-hydroxybenzoate (PHB) moiety, has been studied extensively and found to show a nematic mesophase. The copolyester contains the following segments I and II in addition to PET segments III:



I



II



III

One of these copolymers, containing 60–70 mol% PHB units, shows a maximum in mechanical properties which is superior to the corresponding glass-fibre-reinforced PET, thus representing a kind of molecular composite[86].

Blending liquid-crystalline copolymers with other polymers represents an interesting procedure for applications and for fundamental studies of phase behaviour and properties[87–90a]. When the PHB–PET copolyesters are blended with one other melt-processable polymer, the melt viscosity of such compositions may be much less than that of the melt-processable polymer in the absence of liquid-crystalline copolyester[90b]. The PHB–PET copolymer alone is of interest because it exhibits two amorphous phases: a PET-rich 'flexible' phase and a PHB-rich 'rigid' phase[91].

p-Hydroxybenzoic acid (PHB)–PET copolyester (PHB–PET)/PBT blends. The phase behaviour of (PHB–PET)/PBT as revealed by d.s.c. and by dynamic mechanical measurements is unusual. The T_g of terephthalate-rich copolyester decreased as the PBT ratio was increased. This implies that the terephthalate-rich phase is compatible with PBT. However, the higher of the two T_g values for the copolymer, referred to PHB-rich copolymer, was found to be independent of composition, indicating incompatibility of this phase with PBT. Therefore, the PHB–PET copolymer is considered to be only partially compatible with PBT. With this limited compatibility, the melting point of PBT was not depressed by mixing with the copolymer[75,91].

(PHB–PET)/PET blends. The phase behaviour and compatibility of (PHB–PET)/PET blends have been reported[92–96]. Spinodal demixing of the phases was observable for a blend as prepared by solution blending. Calorimetric analysis shows that the system is incompatible in blends containing 25%, 50% and 75% PHB–PET. Using the dissolution technique, it was also shown that at low PHB–PET levels, the PET is the continuous phase; the PET-rich phase remains the continuous phase until the PHB–PET content reaches 80 wt% in the blend. The thermotropic copolyester does not reach a continuous fibrelike structure until 80% PHB–PET. In any case, the blends show two thermal transition effects, which can be identified as the T_g of the liquid-crystalline polymer phase and the PET phase. It was concluded that there is almost no miscibility of the two phases. There was no significant annealing effect on each of the T_g values, but further annealing at 300 or 325°C decreases the melting temperature from about 249 to 207°C. The authors attributed this phenomenon to transesterification. The crystallization rates of PET in the blends were significantly higher than that of pure PET. The liquid-crystalline polymer appears to act as a nucleating agent for PET[97,98]. No significant transesterification has been reported for this system by Baird *et al.*, as measured by d.s.c.[99]. The residence time in the extruder for blending was only about 1.5 min.

(PHB–PET)/PC blends. To investigate the influence of structure on the miscibility in PC/(PHB–PET) blends, copolyesters with various content of flexible parts in the liquid-crystal polymer chain have been prepared[100]. Compositions of PHB from 10 to 60 mol% were prepared and blended with PC. It was found that the blends exhibited two separate glass transitions. The T_g of PHB–PET remains almost unaltered with increasing PC content, while the T_g of PC is shifted to lower values depending on the amount of PHB–PET in the blend. After annealing at 270°C the T_g values converged in one single T_g at a speed dependent on the PHB–PET

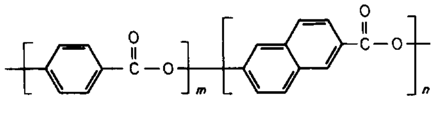
composition[101]. It was suggested that a transesterification occurred, which first resulted in a block formation, further annealing leading to a random copolymer with PHB–PET and PC blocks showing a T_g dependent on composition. A good interphase adhesion between the two polymers was obtained[102].

A related phenomenon has also been found by Nicolais *et al.*[103], namely a progressive shift of the T_g of the PC matrix to lower temperature at increasing PHB–PET content. The authors attributed this effect to the plasticization of the PC by the PET-rich phase of the PHB–PET liquid-crystalline polymer and not to reactions between the two phases of this blend. Morphological studies showed that two distinct phases were recognizable even for the lowest composition utilized, 2% PHB–PET.

A miscible blend was also reported for this system upon solvent casting from a mixed solvent of 60/40 phenol/tetrachloroethane. However, this blend undergoes phase separation during heat treatment, exhibiting a miscibility window, reminiscent of a lower critical solution temperature[104].

(PHB–PET)/poly(hexamethylene terephthalate) (PHMT) blends. PHMT is a higher homologue of the poly(alkylene terephthalate) series. The miscibility of this polyester is significantly affected by the blending technique as reported by other authors[105,106]. Coprecipitated mixtures of PHMT with PHB–PET from 2-chlorophenol solution into methanol form immiscible mixtures. When PHB–PET is the minor component, liquid-crystalline domains are embedded in the matrix. Heat treatment at elevated temperatures creates interactions between the components as indicated by the shift of T_g observed in d.s.c. Reaction in the melt is the cause of the apparent miscibility of PHMT with PHB–PET, and the equilibrium composition of the copolymer is reportedly temperature-dependent[105,106]. The reaction in the melt between the polymers increases the adhesion of the matrix to the embedded domains. High reaction temperatures, small particle size and mixing coupled with particle dispersion and high PHB–PET content in the mixture all promote the melt reaction and decrease the PHMT content in the copolymer formed[105,106].

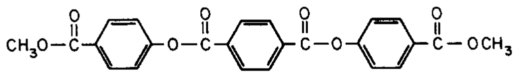
Hydroxybenzoic acid and hydroxynaphthoic acid copolyester (Vectra)/PET blends. Vectra is a commercially available liquid-crystalline polymer from Hoechst Celanese, which has the chemical structure:



Vectra

It has been reported that Vectra/PET blends are immiscible according to the transition temperatures of the blends when little transesterification had occurred[107]. The blend immiscibility superimposed a domain-like structure upon the hierarchical and highly ordered structure of the Vectra. The orientability of the rigid-like liquid-crystalline copolyester is suppressed by the flow of the more viscous random-coil PET. A macroscopic skin–core structure was observed with 25% or more Vectra in the blend. The core and skin are subdivided into a highly defined microscopic substructure of sublayers, which exhibit varying degrees of organization reflecting the composition of the blend and its effect upon the domain size and flow field in the mould.

The phase behaviour of poly(bisphenol E isophthalate-*co*-naphthalate) (BPE/I/N20), containing 40 mol% isophthalate units in a *para*-substituted phenyl ester of terephthalic acid, dimethyl ester liquid crystal (DMELC), has been studied:



DMELC

Two distinct types of phase diagrams have been obtained for binary mixtures of polymers, one containing an in-chain azoxybenzene moiety mixed with *para*-azoxyanisole and one containing a naphthalene unit mixed with a dimethyl ester liquid crystal. These phase diagrams were studied by d.s.c., polarized light microscopy and X-ray diffraction. From this understanding for the physical mixtures, a transesterification reaction was induced incorporating the bifunctional low-molecular-weight liquid crystal into the naphthalene-containing liquid-crystal copolyester. By t.g.a., the thermal stability of an interreacted blend was shown to be superior to that of either individual component in the blend. Thus, a potential new processing technique was revealed, featuring a lower-melting, lower-viscosity blend followed by the incorporation of the dimethyl ester liquid crystal into the copolyester main chain, producing a more rigid, more stable polymer backbone[108].

The phase diagram has been obtained for binary blends of two ester thermotropic liquid crystals. They are poly(bisphenol E isophthalate-*co*-naphthalate) (BPE/I/N20) with a *para*-substituted phenyl ester of terephthalic acid and bis(*p*-(methoxycarbonyl)phenyl)terephthalate[109]. The crystal-to-nematic phase transition has been characterized by transition temperatures and by the Flory–Huggins theory for the melting-point depression of a polymer–diluent system. Transesterification in the solid state was unambiguously proved by d.s.c., t.g.a., polarized light microscopy, X-ray diffraction and dilute-solution viscosity. A catalyst can reduce processing time for production of more rigid, more thermally stable polymers via this novel approach for processing thermotropic liquid-crystalline polymers[109]. During high-temperature processing, increased molecular weight also resulted[110].

PROPERTIES OF POLYESTER BLENDS

All mechanical properties of compatible blends are found to lie near the average values for the pure components. This simple rule is also observed for polyester blends after transreaction. From an applied view, multiphase systems are often desirable. Patents have reported that, with addition of transesterification inhibitors, this reaction has been suppressed, and the melting points of blends show no change[111,112], with stable polyester blends resulting[40].

There are other interesting characteristics about the properties of reactive polyester blends. In PET/PBT blends, a synergistic improvement has been observed in the toughness and the tear strength of films for a PBT concentration of 40% (*Figure 6*). The explanation given is that, owing to reactivity between components, certain amounts of block or graft copolymer cause this property to increase[44].

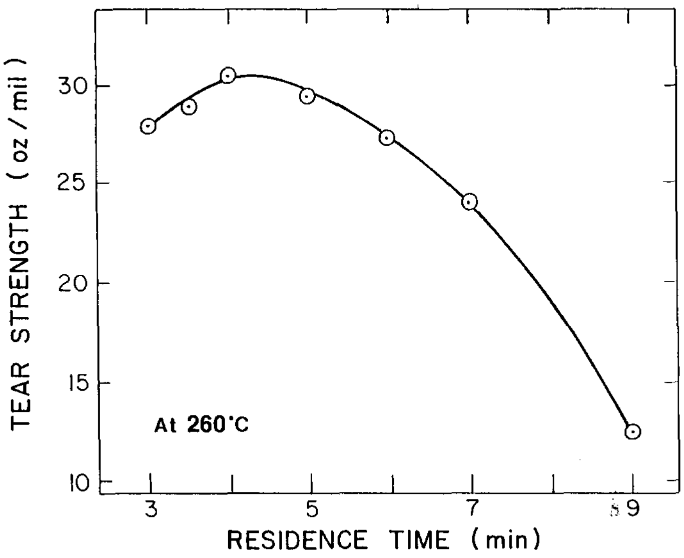


Figure 6 Tear strength in the machine direction of the polyester film based on the PET/PBT (60/40) blend with different residence times in the extruder at 260°C[44] (1 oz/mil ≡ 11.16 kg cm^{-1})

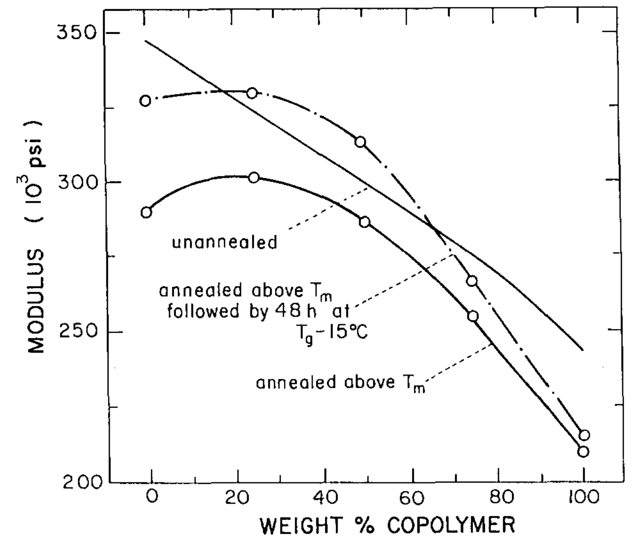


Figure 7 Effect of sub-T_g annealing in a closed mould on modulus of PC/Kodar blends previously reacted above T_m[114] (1 psi ≡ 0.0703 kg cm^{-2})

A related phenomenon has been found in the PC/Kodar blends. As processed, the blends exhibit nearly additive values vs. blend composition for modulus, strength, elongation at failure and notched Izod impact strength. But various annealing protocols caused maxima to appear in plots of modulus and density *versus* composition. Sub-T_g annealing of these blends increased the yield strength. The modulus of injection-moulded specimens was found to develop a maximum at about 75% PC, following such annealing (*Figure 7*). It was also found that, in the mid-composition range, annealing caused a slight increase in modulus[113]. This phenomenon was explained by simultaneous relaxation of volume and molecular orientation. The property relationships in this system are dependent on the method of fabrication.

One purpose of liquid-crystalline polymers in polyester blends is to use the rigid-chain polymer as a molecular reinforcement. The inclusion of 10% PHB-PET has a significant influence on the mechanical properties of a PC matrix[97]. At the spinning temperature of 220°C, PHB-PET fibrils were developed, with a concurrent reduction in the melt viscosity of the PC. A reinforcing effect on modulus was observed. From torsional pendulum measurements it was found that at about 90°C the loss modulus G'' of the blend was located between those of the pure components, but at temperatures above the T_g of PC, they were remarkably higher than those of both components. The torsional modulus of a poly(phenylene sulphide) (PPS)/(PHB-PET) blend (30 wt% PHB-PET) is significantly higher than that for pure PPS film and about 2-3 times higher than for carbon fibre reinforcement[114]. It is to be noted here that the scales of deformation for test of the loss modulus and the tensile modulus are quite different.

CONCLUSIONS

Good progress has been made in the investigation of miscibility among blends of polyesters and polycarbonate. The liquid-crystal copolyester blends have a particularly interesting prospect.

It is noted that the miscibility reported for certain blends has been influenced by transesterification[31,32a]. For other polyester pairs, miscibility is caused directly only by interaction of components[72,74]. Despite the industrial significance of transreaction, for only a few such blends has the process been detailed[54–56]. Even fewer works have reported on the kinetics of transreaction. Relationships are yet to be developed between the degree of transreaction and the role of catalysts, inhibitors, composition, molecular weight, end-group, sequence, etc. Transreaction can occur simultaneously and competitively with polymerization advances and molecular-weight distribution control. Lertola has theoretically derived the transient molecular-weight distribution of a condensation polymer undergoing interchange reaction. It has been concluded that different transient paths are followed under direct and end-group interchange, but that both reactions lead to the equilibrium most-probable distribution[115].

The temperature region for transreaction is about 200-300°C. Below this temperature the rates are even slower, and at higher temperatures other reactions compete: these include the Kolbe rearrangement for the carbonate groups and pyrolysis of ester groups[116]. Crosslinking has been noted[51].

Transreaction can occur in both miscible and immiscible blends. For the latter, the reaction presumably occurs at the interface or in the interfacial regions between the components. The transreaction first produces chains in blocks and then proceeds to an even more random chain composition. As yet, there is no confirmation that reaction occurs exclusively in the amorphous phase or that the presence of a mesophase or crystals has any effect. One work has reported that the kinetic behaviour of these reactions is influenced by the stereochemical structures of carbonyl oxygens on the polymer backbone. Syndiotactic/syndiotactic systems reacted more slowly than syndiotactic/heterotactic and heterotactic/heterotactic systems, respectively[117].

An important postulate was offered early by Lenz and Go[18]; that is, if reaction proceeds below the melting point for any possible sequence that can crystallize, the equilibrium can be shifted to remove the crystallizable units. The documented cases are few and heat treatment may simply cause the apparent similar effect of physical not chemical consolidation of the more crystallizable units. A particular challenge to the crystallization-driven transreaction process is the many copolyesters reported that contain *p*-hydroxybenzoic acid. Crystals of this polymer melt with decomposition near 400°C. This means that formation of crystals of this component would systematically eliminate *p*-hydroxybenzoic acid from the transreaction equilibrium. There seems to be no firm evidence as yet for this effect.

A second challenge to a crystallinity-driven exchange reaction occurs with the polyarylate by itself. It is commonly a 50/50 mixture of iso- and terephthalic acids. The terephthalic acid polymer with bisphenol A is crystallizable with a melting point above 300°C[118]. Yet this crystal has not been reported on heating the polyarylate below this melting point. An obvious possible conclusion is that the increased entropy of random sequences in the chain is the dominant thermodynamic process.

For apparently the same binary blends of PC/PET, one set of workers has shown reaction[31,40] whereas others[43,64] have observed no significant exchange.

For other binary systems, no transreaction has been noted even after prolonged times between 200 and 300°C; including PC/PCL blends[51].

No reaction means the absence of the three commonly proposed ionic transreactions: alcoholysis, acidolysis and mid-chain reaction. The reactions can be accidentally or purposely hindered by impurities or additives[36]. It is unlikely, however, that all chain units could be inhibited. This implies that uncatalysed mid-chain transreaction is probably not a facile nor a common reaction. Nonetheless, direct ester–ester interchange has been considered the most common process for PC–PBT reaction[31,38]. Reaction at chain ends is a more probable process, if of appropriate composition and catalysis. A question is whether phenolic and acid end-groups can both catalyse and participate in reaction. It is presumed that the chain ends can react if they are in appropriate acid–base ratios.

In addition to acid or base, and transition-metal catalysts, compounds such as those of tungsten are known to activate both polymerization and transreaction. Removal of trace residual catalyst has been shown to stop or reduce the reaction[31].

Alternatively, a host of compounds, particularly of phosphorus, are known to inhibit transreaction[32–35]. It has been postulated that phosphates complex the residual trace metals that catalyse transreaction[56]. Phosphate addition alone appears to be insufficient to stop transreaction. Hydrolysis into species such as diphosphonates may be required to provide a transreaction suppressant. Since this simultaneously removes water, the inhibition process may be dual. The role of trace water in transreaction is expected to be real, yet at present unknown. Any polymerization advance can produce water, which in turn may affect transreaction.

In the present review, the transesterification discussed mainly takes place in the main chains. Transreaction between polymers containing pendant ester groups has also been reported and used as a new way to modify thermoplastic polymers[119–121].

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